



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 289 599
A1

(12)

EUROPEAN PATENT APPLICATION

published in accordance with Art. 158(3) EPC

(21) Application number: 86904351.3

(51) Int. Cl.: H 01 F 1/08, H 01 F 41/02

(22) Date of filing: 27.06.86

Data of the international application taken as a basis:

(86) International application number:
PCT/JP 86/00327

(87) International publication number:
WO 88/00387 (14.01.88 88/2)

(43) Date of publication of application: 09.11.88
Bulletin 88/45

(71) Applicant: NAMIKI PRECISION JEWEL CO., LTD., 8-22,
Shinden 3-chome, Adachi-ku Tokyo 123 (JP)

(72) Inventor: IMAIZUMI, Nobuo, 1259-2-301, Misawa,
Hino-shi Tokyo 191 (JP)

(84) Designated Contracting States: DE FR

(74) Representative: Bunke, Holger, Dr. et al, Patentanwälte
Prinz, Leiser, Bunke & Partner Manzingerweg 7,
D-8000 München 60 (DE)

(54) PROCESS FOR PRODUCING PERMANENT MAGNETS.

(57) A process for heat-treating of rare earth permanent magnets chiefly of the Nd-Fe-B system. In the permanent magnet easily oxidized in the open air, an alloy thereof is pulverized, orientated compression-molded in a magnetic field or compression-molded in a non-magnetic field, and sintered at 900° to 1200 °C, then ground and polished into a practical shape, subjected to solution heat treatment at 900° to 1200 °C in an atmosphere of oxygen and/or nitrogen, or aged at 300° to 900 °C, so that an oxide and/or a nitride film of 0.001 to 10 µm in thickness is formed on the surface of the magnet in order to prevent the oxidation and to remove work strain.

EP 0 289 599 A1

SPECIFICATION

Process for producing permanent magnets

FIELD OF THE INVENTION

This invention concerns a heat treatment method for rare-earth type permanent magnets, principally those of the Nd-Fe-B variety.

BACKGROUND OF THE INVENTION

Since the discovery that there would be theoretically very high magnetic properties $[(BH)_{\max} \sim 50 \text{MGOe}]$ when rare-earth metals and transition metals are combined into metal compounds in a ratio of 2:17 to form a rare-earth transition metal alloy, there have been a number of attempts to obtain practical permanent magnet applications using these types of compounds. One example is the Sm-Co-Cu-Fe intermetallic compound where $(BH)_{\max}$ has reached $\sim 30 \text{MGOe}$. Further, with Nd-Fe intermetallic compounds, high magnetic properties of $(BH)_{\max} \sim 40 \text{MGOe}$ have been reached. These alloy formulations are crushed into powder, and then aligned and compression formed in a magnetic field, or compression formed in a non-magnetic field, sintered, solution treated and aged to form a mass, and then ground and polished into permanent magnets of the shape required according to the most usual methods of their preparation. Since the rare-earth and ferrous type permanent magnets, particularly the R-Fe-M permanent magnets (where R represents one or more types of

rare-earth metals, and M represents B or other metalloid element), are easily oxidized when exposed to air, when they are used in precision applications, such as in miniature electronic parts for magnetic circuits using permanent magnets, there are many instances where oxidation caused by exposure of the magnet to air leads to a degradation of the magnetic properties and fluctuations in their permanence due to changes in the magnetic space. Because of this, the prior art has used Cr or Ni wet type plating to cover the surface to prevent this oxidation.

When the wet type plating means are used, however, the surface of the permanent magnet itself can be corroded by the degreasing and oxidation removal processes, which makes plating difficult. In addition, following the plating operation, gaps sometimes exist between the permanent magnet surface and the plating layer. Peeling of the plating is likely in these areas. Also, it is a defect that rust is easily formed on pinholes. It was found that demagnetization curve is deformed as shown in Fig.1-A, because overall magnetic properties were affected by degraded magnetic properties on surface layer, as machining strain were formed on the machined surface layer, which were ground and polished to obtain the desired shape, after having its final magnetic properties through sintering, solution treating and aging. These phenomena are especially dramatic in permanent magnets

which have a relatively small volume but a relatively large surface area. Such defects result in lower production yields.

In consideration of this regard, the objects of this invention are to keep surface adhesiveness without affecting active based body and to promote magnetic properties reduced by machining strain on surface layer.

DISCLOSURE OF THE INVENTION

This invention concerns a permanent magnet alloy conforming to the general formula: $R(T,M)_z$ (where R represents one or a mixture of two or more rare-earth metals, T is transition metals such as Fe or Co, M is a metalloid element such as B, and z is 4 to 9) where the alloy is crushed and aligned and compression formed in a magnetic field or compression formed in a non-magnetic field to form the green body. Then first, for permanent magnets having a small surface area/volume ratio, they are sintered at a temperature of 900 to 1200°C, then machined into appropriate shapes, and then solution treated at 900 to 1200°C in a 10^{-8} to 1 Torr gas atmosphere, after which they are aged at 300 to 900°C. Secondly, for permanent magnets having a large surface area/volume ratio, they are sintered at 900 to 1200°C, solution treated at 900 to 1200°C, machined into appropriate shapes, and then aged in a gas atmosphere of 10^{-8} to 1 Torr at 300 to 900°C. Thirdly, they can be sintered at 1000 to 1200°C, machined into appropriate shapes, re-sintered in a 10^{-8} to 1

Torr gas atmosphere at 1000 to 1200°C, in order to manufacture these permanent magnets. The gas environment used for these various processes may be oxygen, nitrogen or a mixture; it is desirable that the surface layer be less than 10µm in thickness. When heating, if the amount of oxygen and/or nitrogen in the atmosphere is less than 10^{-8} Torr, then a surface layer will not be formed, or, if there is more than 1 Torr, then the oxide and/or the nitride layer will become skin-like and cause degradation of the magnetic properties of the permanent magnets themselves. Also, if heated to a temperature of under 300°C, formation of the surface layer will not take place. If a temperature of 1200°C is exceeded, then oxygen and/or nitrogen will disperse into the interior of the permanent magnet and magnetic properties will be drastically reduced. Accordingly, under these conditions, it is not desirable for a surface layer thickness of 10µm to be exceeded, because of oxide or nitride skin-like layer be formed. The reason for the limitation placed on the temperature is to eliminate strain layers from machining in the final product and to promote the maintenance of coercive force. In other words, with the sintering, solution treating and aging processes, the appropriate temperature ranges are: 900 to 1200°C, 900 to 1200°C and 300 to 900°C, respectively. If any of those ranges are not observed, the result will be a degradation of magnetic

properties, or strain layers resulting from machining which depart from this invention.

In this invention, the oxygen causes the formation of black-colored rust layer on the surface of the permanent magnet which prevents further oxidation and allows it to be stable in the air. When nitrogen is used, a similar effect is observed, and one of the objectives of this invention, preventing rust, is thereby realized.

At the same time, by accomplishing the heat treatment according to this invention, following grinding and polishing after the sintering has taken place, any machining strain that was induced can be eliminated during the aging process, therefore coercive force is especially promoted wherein the magnetic properties of surface layer are reduced.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows a demagnetization curve for permanent magnet.

A: for the production method of the prior art involving sintering, solution treating, aging and machining for the permanent magnets.

B: for the production method of this invention where there is sintering, machining, solution treating and aging for the permanent magnets.

Fig. 2 shows an Auger spectral analysis of a magnet prepared according to this invention. It indicates the

concentration distribution in the direction of the layer thickness.

BEST MODE OF CARRYING OUT THE INVENTION

Below, examples of some of the best mode of carrying out this invention will be described.

EXAMPLE 1:

A formulation of $\text{Nd}(\text{Fe}_{0.9}\text{B}_{0.1})_5$ alloy was melted, roughly crushed, finely crushed and formed in a magnetic field to prepare the green body for the magnet. It was sintered at a temperature of 1080°C to obtain a 9mm square sintered block. Next this sintered block was grinding to dimensions of 8mm square, after which it was solution treated in a 10^{-6} Torr oxygen partial pressure atmosphere at 1050°C for 30min., and then it was cooled to room temperature. Next, it was aged at 600°C for 60 min.; this was called sample A. On the other hand, the same type of sintered block was aged prior to grinding it. This, sample B, was then grinding to 8mm block. Table 1 shows the magnetic properties of sample A and B.

	A	B
Br (KG)	11.6	11.6
$i H_c$ (KOe)	10.5	10.4
(BH)max(MG·Oe)	31.7	30.5

TABLE 1

Sample A and B were left in a 95% humidity, 65°C

environment and were checked for corrosion. On the processed surfaces of sample B, a red-colored rust appeared, but only a small amount of red-colored rust was observed around the perimeter edges of sample A; there was no change at all to the processed surface areas.

EXAMPLE 2:

A Nd-Fe-B alloy was melted and cast into an ingot. A vibrating mill was then used to crush it into 5 to 20 μ m powder. This was then compressed in a magnetic field and then formed into blocks which were sintered for an hour in a vacuum at 1120°C. The resulting blocks were divided into samples A and B. The sample A was then processed according to methods of the prior art: solution treatment for 1 hour at 1100°C followed by aging at 600°C for an hour and grinding to the proper dimensions to form the permanent magnet. Sample B was then processed according to this invention. It was ground to the same dimensions and shape, and then solution treated at 1100°C for 1 hour, and then aged at 600°C for an additional hour. The demagnetization curves of the respective magnets were measured. As shown in Fig.1, Sample A had a wavy curve, while B showed a good curve with a sharp shoulder.

EXAMPLE 3:

$\text{Nd}_{0.8}\text{Pr}_{0.1}\text{La}_{0.05}\text{Dy}_{0.05}(\text{Fe}_{0.92}\text{B}_{0.08})_6$ alloy was used to make the green body as in EXAMPLE 1. Sintering then

took place at temperatures of 1050, 1100 and 1200°C respectively to obtain sintered blocks 9mm square. These ground to 8mm square blocks, and then they were solution treated in an atmosphere mixed oxygen and nitrogen in a 1:4 ratio at 10^{-3} Torr for 30 minutes at temperature of 1050, 1000 and 900°C respectively. Then, they were aged in this same atmosphere for 60 minutes at 600°C to prepare sample (samples No. 1 through 9). Then these, along with samples made according to the prior art method (samples No. 10 through 12) were measured for their magnetic properties [maximum energy products: (BH) (MGOe)], and after having been left to stand at 60°C in 90% humidity for 100 hours, the appearance of any rust was observed. TABLE 2 shows the results.

No.	Heat treatment (°C), machining process order	(BH)	*
1	1,050 → machining → 1,050 → 600	33.5	⊙
2	1,050 → machining → 1,000 → 600	34.0	⊙
3	1,050 → machining → 900 → 600	33.0	⊙
4	1,100 → machining → 1,050 → 600	34.5	⊙
5	1,100 → machining → 1,000 → 600	34.0	⊙
6	1,100 → machining → 900 → 600	34.2	⊙
7	1,150 → machining → 1,050 → 600	35.0	⊙
8	1,150 → machining → 1,000 → 600	35.2	⊙
9	1,150 → machining → 900 → 600	34.0	⊙
10	1,100 → 1,050 → 600 → machining	32.0	x
11	1,100 → 1,000 → 600 → machining	31.5	x
12	1,100 → 900 → 600 → machining	31.7	x

⊙: No change

* x: Rust all over the surface

TABLE 2

EXAMPLE 4:

Sintered blocks were prepared as in EXAMPLE 3, and after solution treating, the samples were ground into 8mm blocks and aged. The magnetic properties were measured for these samples [maximum energy products: (BH) (MGOe)], and after leaving in a 60°C 90% humidity environment for 100 hours, the appearance of any rust was observed.

Those results appear in TABLE 3.

NO.	Heat treatment (°C), machining process order	(BH)	*
13	1,050 → 1,050 → machining → 600	35.0	◎
14	1,050 → 1,000 → machining → 600	34.8	○
15	1,050 → 900 → machining → 600	33.2	○
16	1,100 → 1,050 → machining → 600	35.0	◎
17	1,100 → 1,000 → machining → 600	35.0	◎
18	1,100 → 900 → machining → 600	32.8	○
19	1,150 → 1,050 → machining → 600	34.8	◎
20	1,150 → 1,000 → machining → 600	34.5	◎
21	1,150 → 900 → machining → 600	33.6	○

◎ : No change

* ○ : Non-continuous rust on edges

TABLE 3

EXAMPLE 5:

An alloy composed of $\text{Nd}_{0.9}\text{Dy}_{0.1}(\text{Fe}_{0.81}\text{Co}_{0.1}\text{B}_{0.09})_{5.8}$ was sintered as in EXAMPLE 1 and ground into 8mm square blocks. Next, the blocks were solution treated in a mixed gas atmosphere of oxygen : nitrogen = 1:4 under various partial pressures, and then they were aged. These samples were

then tested for magnetic properties [maximum energy products: (BH) (MGOe)] and the appearance of rust after letting them stand at 60°C and 90% humidity for 100 hours. The results appear in TABLE 4.

TABLE 4

No.	Mixed gas partial pressure (Torr)	(BH)	*
22	5×10^{-8}	38.5	\triangle
23	2×10^{-6}	38.6	o
24	5×10^{-3}	38.3	\odot
25	1×10^{-1}	35.2	\odot
26	1	30.4	o

* \odot : No change

o : Non-continuous rust on edges

\triangle : Continuous rust on edges

As is clear from TABLE 4, when the gas partial pressure is low, there is an undesirable weakness rust protective layer on the surface. Also, if the gas pressure is too high, oxygen and nitrogen permeate to the inside of the magnet, not just the surface, causing the original magnetic properties to decline.

EXAMPLE 6:

An alloy formulation of $\text{Nd}_{0.9}\text{Dy}_{0.1}(\text{Fe}_{0.92}\text{B}_{0.08})_{5.8}$ was sintered, ground, solution treated and aged as in EXAMPLE 1. Auger spectro-graphy was used to assess the surface condition. Fig. 2 shows the concentration distribution of O_2 and N_2 in the thickness direction of the surface layer. As can be seen from Fig. 2, nitrogen and oxygen are captured to a depth

of 10^3 to 10^4 Å from the surface of the magnets. When these samples were left to stand for 100 hours at 60°C and 90% humidity, almost no rust was noted.

As described above, by using the surface treatment method of this invention in permanent magnets, superior corrosion protection is realized and there is a strong bond between the protective layer and the magnet. Also, since it is very easy to control the coating layer, this process is appropriate for precision parts applications in miniature electronic circuits. This process provides both mechanical and cost advantages over those processes used in the prior art, and the aging process in this invention also works to relieve any machining strain in the surface layer from grinding and polishing, so that coercivity is improved and machining strain is eliminated through the heating in the aging process. This helps damaged surface layers to return to their normal structure.

CLAIMS

(1) A process for producing permanent magnets from a permanent magnet alloy powder of general formula: $R(T,M)_z$ (where R is one or a mixture of two or more rare-earth metals, T is Fe, Co or other transition metal, and M is a metalloid such as B, and $z = 4$ to 9), where the powder is aligned and compression formed in a magnetic field or compression formed in a non-magnetic field to come up with the green body, and then, after sintering at 900 to 1200°C, it is machined into a utilizable shape, and then after solution treating at a temperature of 900 to 1200°C in a gas atmosphere of 10^{-8} to 1Torr, it is aged at 300 to 900°C.

(2) A process for producing permanent magnets according to CLAIM (1) wherein the gas atmosphere is mixture of oxygen and nitrogen.

(3) A process for producing permanent magnets according to CLAIM (1) wherein the gas atmosphere is oxygen.

(4) A process for producing permanent magnets according to CLAIM (1) wherein the gas atmosphere is nitrogen.

(5) A process for producing permanent magnets according to CLAIM (1) wherein an oxide or nitride layer is formed which is 0.001 to 10 μ m thick.

(6) A process for producing permanent magnets from a permanent magnet alloy powder of general formula: $R(T,M)_z$ (where R is one or a mixture of two or more rare-earth metals,

T is Fe, Co or other transition metal, and M is a metalloid such as B, and $z = 4$ to 9), where the powder is aligned and compression formed in a magnetic field or compression formed in a non-magnetic field to come up with the green body, and then, after sintering at 900 to 1200°C, it is solution treated at a temperature of 900 to 1200°C, then machined into a utilizable shape, and then is aged at 300 to 900°C in a gas atmosphere of 10^{-8} to 1 Torr.

(7) A process for producing permanent magnets according to CLAIM (6) wherein the gas atmosphere is mixture of oxygen and nitrogen.

(8) A process for producing permanent magnets according to CLAIM (6) wherein the gas atmosphere is oxygen.

(9) A process for producing permanent magnets according to CLAIM (6) wherein the gas atmosphere is nitrogen.

(10) A process for producing permanent magnets according to CLAIM (6) wherein an oxide or nitride layer is formed which is 0.001 to 10 μ m thick.

(11) A process for producing permanent magnets from a permanent magnet alloy powder of general formula: $R(T,M)_z$ (where R is one or a mixture of two or more rare-earth metals, T is Fe, Co or other transition metal, and M is a metalloid such as B, and $z = 4$ to 9), where the powder is aligned and compression formed in a magnetic field or compression formed in a non-magnetic field to come up with the green body, and

- 14 -

then, after sintering at 900 to 1200°C, it is machined into a utilizable shape, and then re-sintered at temperature of 900 to 1200°C in a gas atmosphere of 10^{-8} to 1 Torr.

(12) A process for producing permanent magnets according to CLAIM (11) wherein the gas atmosphere is mixture of oxygen and nitrogen.

(13) A process for producing permanent magnets according to CLAIM (11) wherein the gas atmosphere is oxygen.

(14) A process for producing permanent magnets according to CLAIM (11) wherein the gas atmosphere is nitrogen.

(15) A process for producing permanent magnets according to CLAIM (11) wherein an oxide or nitride layer is formed which is 0.001 to 10 μ m thick.

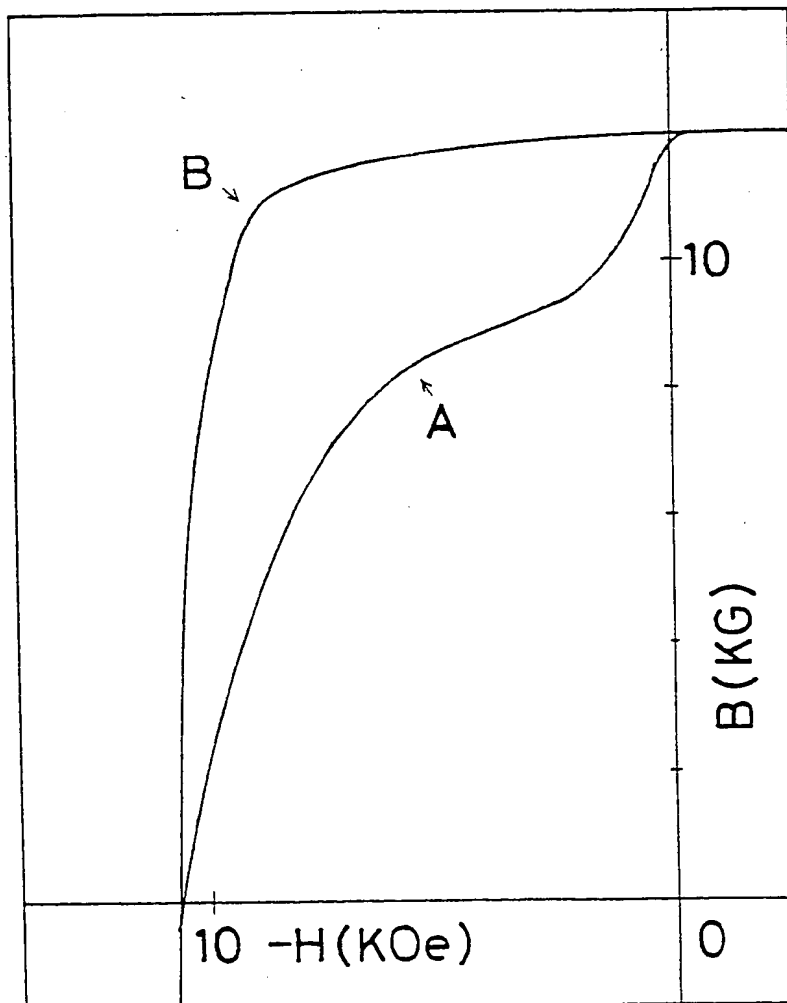
$\frac{1}{2}$ 

Fig.1

0289599

$2/2$

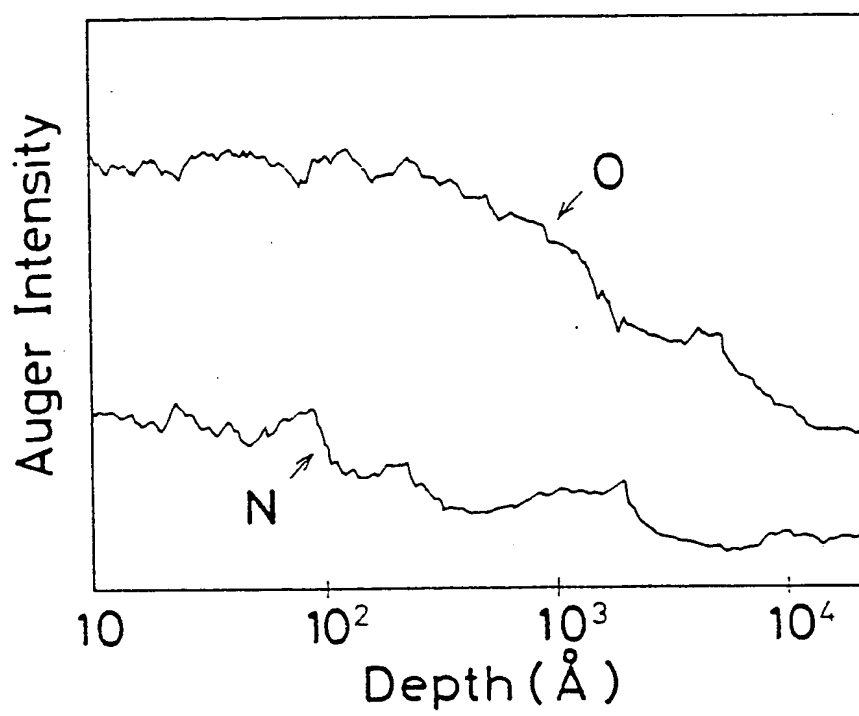


Fig. 2

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/JP86/08327 0289599

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ¹		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl ⁴ H01F1/08, H01F41/02		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
IPC	H01F1/08, H01F41/02	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁴		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹¹		
Category ¹	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹⁴
A	JP, A, 59-64739 (General Motors Corp.) 12 April 1984 (12. 04. 84) (Family: none)	1 - 15
A	JP, A, 59-217304 (Sumitomo Tokushu Kinzoku Kabushiki Kaisha) 7 December 1984 (07. 12. 84) (Family: none)	1 - 15
A	JP, A, 60-15904 (Suwa Seikosha Kabushiki Kaisha) 26 January 1985 (26. 01. 85) (Family: none)	1 - 15
A	JP, A, 60-34005 (Sumitomo Tokushu Kinzoku Kabushiki Kaisha) 21 February 1985 (21. 02. 85) (Family: none)	1 - 15
A	JP, A, 60-54406 (Sumitomo Tokushu Kinzoku Kabushiki Kaisha) 28 March 1985 (28. 03. 85) (Family: none)	1 - 15
A	JP, A, 60-63902 (Sumitomo Tokushu Kinzoku Kabushiki Kaisha) 12 April 1985 (12. 04. 85) (Family: none)	1 - 15
<p>¹ Special categories of cited documents: ¹¹</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"Z" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ²		Date of Mailing of this International Search Report ²
August 26, 1986 (26. 08. 86)		September 8, 1986 (08. 09. 86)
International Searching Authority ³		Signature of Authorized Officer ²⁰
Japanese Patent Office		

